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SYNTHESIS AND MOLECULAR STRUCTURE OF CLOSO-3-(ETA
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ANGELES DEPT OF CHEMISTRY AND BIOCHEMISTR..
H C KANG ET AL. 25 JUN 87 TR-129

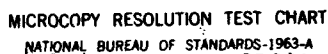
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Synthesis and Molecular Structure of
closo-3-(η^6 -CH₃C₆H₅)-3,1,2-FeC₂B₉H₁₁ and
closo-3-(η^6 -1,4-(CH₃)₂C₆H₄)-3,1,2-FeC₂B₉H₁₁

by

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) The reaction of $\text{K[nido-7,8-C}_2\text{B}_9\text{H}_{12}]$ with ferric chloride and triethylamine in ether toluene or <i>p</i> -xylene solution afforded neutral mixed sandwich (arene)ferracarborane complexes $\text{closo-3-(}\eta^6\text{-CH}_3\text{C}_6\text{H}_5\text{)-3,1,2-FeC}_2\text{B}_9\text{H}_{11}$ (1) or $\text{closo-3-(}\eta^6\text{-1,4-(CH}_3\text{)}_2\text{C}_6\text{H}_4\text{)-3,1,2-FeC}_2\text{B}_9\text{H}_{11}$ (2), respectively. The molecular structures of the complexes have been determined from single-crystal X-ray diffraction data. Both ferracarboranes adopt a closo geometry for the $\text{d}_1\text{MC}_2\text{B}_9$ icosahedra. The arene rings occupying the other coordination sites of Fe are planar and nearly parallel to the C_2B_3 plane of the carborane ligand. Complex 1 crystallized in 1, the monoclinic space group $\text{P2}_1/\text{c}$ with $a = 7.7452(7)$, $b = 8.8974(9)$, $c = 19.6596(20)$ Å, $\beta = 90.195(3)^\circ$, $V = 1355$ Å ³ and $Z = 4$. Complex 2 crystallized in the orthorhombic space group Pna2_1 with $a = 12.862(3)$, $b = 7.491(2)$, $c = 15.002(3)$ Å, $V = 1445$ Å ³ and $Z = 4$. | | | | | |
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Synthesis and Molecular Structure of
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Abstract

The reaction of K[nido-7,8-C₂B₉H₁₂] with ferric chloride and triethylamine in either toluene or *p*-xylene solution afforded neutral mixed sandwich (arene)ferracarborane complexes *closo*-3-(η^6 -CH₃C₆H₅)-3,1,2-FeC₂B₉H₁₁ (1) or *closo*-3-(η^6 -1,4-(CH₃)₂C₆H₄)-3,1,2-FeC₂B₉H₁₁ (2), respectively. The molecular structures of the complexes have been determined from single-crystal X-ray diffraction data. Both ferracarboranes adopt a *closo* geometry for the d⁶ MC₂B₉ icosahedra. The arene rings occupying the other coordination sites of Fe are planar and nearly parallel to the C₂B₃ plane of the carborane ligand. Complex 1 crystallized in the monoclinic space group *P2₁/c* with *a* = 7.7452(7), *b* = 8.8974(9), *c* = 19.6596(20) Å, β = 90.195(3)°, *V* = 1355 Å³, and *Z* = 4. Complex 2 crystallized in the orthorhombic space group *Pna2₁* with *a* = 12.862(3), *b* = 7.491(2), *c* = 15.002(3) Å, *V* = 1445 Å³, and *Z* = 4.

Synthesis and Molecular Structures of
***closo*-3-(η^6 -CH₃C₆H₅)-3,1,2-FeC₂B₉H₁₁ and**
***closo*-3-(η^6 -1,4-(CH₃)₂C₆H₄)-3,1,2-FeC₂B₉H₁₁**

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The chemistry of mixed-sandwich transition metal complexes of the type $[(\eta^6\text{-arene})M(\eta^5\text{-Cp})]$ has been well documented in the literature.¹ In view of the close structural and electronic similarity of the dicarbollide ligand to that of the cyclopentadienyl ligand,² the former would be expected to form analogous mixed ligand complexes with arenes and transition metals. However, only a few of these complexes have been reported.³ As part of our ongoing investigation of metallocarborane derivatives, we have prepared (η^6 -arene)ferracarborane complexes incorporating toluene; *closo*-3-(η^6 -CH₃C₆H₅)-3,1,2-FeC₂B₉H₁₁ (1), or *p*-xylene; *closo*-3-(η^6 -1,4-(CH₃)₂C₆H₄)-3,1,2-FeC₂B₉H₁₁ (2), directly from the reactions of K[nido-7,8-C₂B₉H₁₂], ferric chloride and triethylamine in either toluene or *p*-xylene solution. This simple route for the formation of (η^6 -arene)ferracarborane was originally employed for the synthesis of boron-substituted carborane cage derivatives using ferric chloride promoted oxidative coupling of K[nido-7,8-C₂B₉H₁₂] with Lewis base L.⁴



Both a symmetrically and an asymmetrically substituted zwitterionic neutral carborane,⁵

nido-10- $\text{N}(\text{C}_2\text{H}_5)_3$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ⁶ and *nido*-9- $\text{N}(\text{C}_2\text{H}_5)_3$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ⁷ were found in the above reaction mixture and characterized by spectroscopic techniques. While complexes 1, 2 and triethylamine-substituted neutral species were obtained in low yield, the known complex $[\text{Fe}^{\text{III}}(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})_2]^{2+}$ (3)^{2b} was afforded as a major product. The basicity of triethylamine is apparently sufficient to deprotonate the *nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{12}^-$ ion to form a dicarbollide *nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ which functions as a ligand in these complexes. When less basic nitrogen-containing ligands such as pyridine and acetonitrile were employed in this reaction, ligand substituted neutral carboranes were exclusively formed in high yields.⁸ When ferrous chloride was used instead of ferric chloride in this reaction, only the iron sandwich complex 3 was detected. This result suggests that the formation of 1 and 2 may take place while Fe^{2+} ion is supplied slowly in small amounts from the oxidative substitution reaction as a reduced species. The complexes 1 and 2 are thermally stable neutral orange crystals, although their solutions show color change after exposure to air for three days. Their ¹¹B FT NMR spectra are consistent with those of other η^6 -arene metallacarborane complexes of MC_2B_9 ,^{3a} showing a relative area ratio 1:1:2:2:2:1. In ¹H FT NMR spectra, the peaks assigned to the aromatic ring protons exhibit the upfield shift which has been found for the protons of the complexed arenes.⁹

The structure of 1 was determined by a single crystal X-ray diffraction study and the molecule is illustrated in Figure 1. Selected interatomic distances and angles are listed in

Figure 1

Table I. Due to the disorder present in the crystal, the bond distances and angles in the

Table I

toluene ligand in species 1 could not be determined accurately. Thus, we decided to obtain the structure of the closely related complex 2. The molecular structure of 2 is illustrated in Figure 2 and selected interatomic distances and angles are listed in Table II. As can be seen

Figure 2

Table II

in the figures, the structures of **1** and **2** exhibit a similar sandwich type geometry with the iron flanked by both the arene ring and the C_2B_3 face of the C_2B_9 cage. C_2B_3 bonding faces in **1** and **2** are planar (maximum deviation; 0.023 Å and 0.015 Å, respectively) with the iron approximately centered over the ring at distances of 1.494 Å and 1.480 Å, respectively, from the C_2B_3 plane.¹⁰ The iron atom is also bound in a symmetrical fashion to the arene ring in **1** and **2** with distances of 1.566 Å and 1.575 Å from the C_6 plane,¹¹ respectively. The C_6 arene rings in **1** and **2** are also planar (maximum deviation in **2**; 0.016 Å) and almost parallel to the C_2B_3 plane with dihedral angles 1.8° and 2.2°, respectively.¹² The average Fe-C (arene) distances of 2.098(20) Å in **1** and 2.115(9) Å in **2** are similar to those of other *closo*- FeC_2B_9 arene complexes; e.g. 2.116(10) Å in *closo*-2-(η^6 -CH₃C₆H₅)-1,7-(CH₃)₂-2,1,7- $FeC_2B_9H_9$ ¹³ and 2.123(14) Å in *closo*-3-(η^6 -(CH₃)₃C₆H₃)-3,1,2- $FeC_2B_9H_{11}$,^{3a} and slightly longer than the average distance of 2.038(9) Å in the smaller cage complex 1-(η^6 -CH₃C₆H₅)Fe-2,3-(C₂H₅)₂C₂B₄H₄.^{3c}

The orientation of the arene rings with respect to the carborane ligand is of interest and in Figure 3, the arene and the C_2B_3 rings of the carborane ligands in each molecule are

Figure 3

projected onto a common plane. Both the C_6 rings are staggered with respect to the carbon-carbon edge (C(01)-C(02)). In molecule **1** the C_6 ring is eclipsed with respect to one of the boron-boron edges (B(04)-B(08)); however, in molecule **2** the arene ring shows a nearly eclipsed arrangement to the other boron-boron edge (B(07)-B(08)). The orientation of the methyl groups precludes any possible symmetry in either molecule, although the methyl groups were expected to lie between the carbon-carbon edge of the C_2B_3 face. The fact that the orientation of one of the methyl groups of xylene in **2** and the methyl group of toluene in **1** is similar, suggests that they are energetically similar and that they utilize their most favorable conformations. There are no significant intermolecular contacts in either crystal structure.

Experimental Section.

All manipulations were carried out in an inert atmosphere with standard Schlenk techniques.¹⁴ All solvents were purified by standard procedures and distilled under nitrogen prior to use. Triethylamine was distilled before use. Infrared spectra were recorded using KBr pellets on a Beckman Model FT 1100 FT-IR. ¹H NMR spectra were obtained using a Bruker WP-200 FT-NMR spectrometer at 200.133 MHz. ¹¹B NMR spectra were recorded on a Bruker AM-500 FT-NMR spectrometer at 160.463 MHz. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Preparation of *closo*-3-(η^6 -CH₃C₆H₅)-3,1,2-FeC₂B₉H₁₁ (1). A 1-L three-neck flask was fitted with a reflux condenser having a gas outlet, a pressure equalized addition funnel and a gas inlet which was connected to a nitrogen manifold. To the flask were added 1.07 g (6.2 mmol) of K[*nido*-7,8-C₂B₉H₁₂] along with 50 mL of toluene, 11 mL of triethylamine and a magnetic stir bar. The solution was heated to reflux and a solution of 2.10 g (13 mmol) of anhydrous ferric chloride in 400 mL of toluene was added dropwise over a period of 1 hr to the refluxing solution. The color of the solution slowly changed to dark red. After approximately 15 hr of reflux, the reaction mixture was cooled and filtered, and the precipitate washed with 100 mL of hot benzene. The combined red filtrates were washed with 200 mL portions of distilled water 3 times. The washed toluene solution was dried over anhydrous magnesium sulfate, evaporated *in vacuo* to a volume of 20 mL, and then let stand for a period of one week. Brown rod-shape crystals were formed (0.035 g, 3 % yield). ¹H NMR (ppm, reference residual solvent protons = 5.32, CD₂Cl₂, 298 K): 6.2 (m, 3H, aromatic protons), 6.0 (m, 2H, aromatic protons), 3.8 (s, 2H, carborane CH), 2.5 (s, 3H, CH₃). ¹¹B NMR (ppm, reference BF₃·OEt₂, THF, 298 K): 0.1, -3.1, -9.9, -11.1, -21.2, -26.3 (1:1:2:2:2:1).

Preparation of *closo*-3-(η^6 -1,4-(CH₃)₂C₆H₄)-3,1,2-FeC₂B₉H₁₁ (2).

The trimethylammonium salt of [*nido*-7,8-C₂B₉H₁₂]⁻ (3.10 g, 15 mmol), anhydrous ferric

chloride (2.43 g, 15 mmol) and 20 mL of triethylamine were treated with *p*-xylene in a manner similar to that described above. Orange crystals were obtained (0.15 g, 5.1 % yield). Anal. Calcd for $C_{10}H_{21}B_9Fe$: C, 40.79; H, 7.19; B, 33.05; Fe, 18.97. Found: C, 40.58; H, 6.91; B, 31.71; Fe, 18.42. IR: 3039(w), 2613(m), 2530(vs, br), 1489(m), 1452(w), 1375(m), 1106(w), 1016(s), 987(s), 865(w) cm^{-1} . 1H NMR (ppm, CD_2Cl_2 , 298 K): 5.9 (s, 4H, aromatic protons), 3.6 (s, 2H, carborane CH), 2.4 (s, 6H, CH_3). ^{11}B NMR (ppm, reference $BF_3 \cdot OEt_2$, THF, 298 K): 0.8, -3.0, -9.4, -10.2, -20.6, -25.6 (1:1:2:2:2:1).

Collection and Reduction of X-ray Data for 1. An air-stable crystal, obtained from toluene solution, was mounted on a thin glass fiber on a diffractometer constructed by Professor C. E. Strouse of this department. Systematic absences were found for reflections $0k0$, $k = 2n + 1$, and for $h0l$, $l = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 43 accurately centered reflections ($9.5^\circ < 2\theta < 20.5^\circ$). These dimensions and other parameters, including conditions of data collection, are summarized in Table III. Data were collected in the $\theta - 2\theta$ scan mode. Three intense reflections (2,0,6), (2,0,-6), and (2,3,-1) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, $ca \pm 4\%$, during the course of the experiment. Of the 2386 unique reflections measured, 1588 were considered observed ($I > 3 \sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization, but not for absorption effects. Programs used in this work include locally modified versions of the programs listed in the reference section.¹⁵

Solution and Refinement of the Structure of 1. Atoms were located by use of the heavy-atom method. Although they are not quite identical, reflections hkl and $hk-l$ are similar in magnitude. Fe lies approximately in a "mirror" plane which bisects the C_2B_9 icosahedron giving positional overlap with large thermal ellipsoids. The arene is disordered about this plane. All calculations were performed on the VAX 11/750 crystallographic

computer. All carborane hydrogen atoms were kept in located positions and all arene hydrogen atoms were included in calculated positions, C-H = 1.0 Å, with assigned u values of 0.04 and 0.11 Å² for cage and ring and for methyl H, respectively. Anisotropic thermal parameters were refined for Fe and for cage non-hydrogen atoms. The arene was refined in 2 positions with occupancies x and $1-x$ which refined to about 60/40. Each arene ring was constrained to be a rigid hexagon, C-C = 1.395 Å, and each methyl group was constrained to be tetrahedral, H-C-H = 109.5°. Scattering factors for H were obtained from Stewart *et al.*¹⁶ and for other atoms were taken from The International Tables for X-ray Crystallography.¹⁷ Anomalous dispersion terms were applied to the scattering of Fe. A final difference electron density map was essentially featureless, the maximum and minimum peaks being about 0.7 e/Å³. Final positional and thermal parameters for non-hydrogen atoms are given in Table IV.

Collection and Reduction of X-ray Data for 2. An air-stable crystal, obtained from THF/heptane solution, was mounted on a thin glass fiber on a diffractometer constructed by Professor C. E. Strouse of this department. Systematic absences were found for reflections $0kl$, $k + l = 2n + 1$, and for $h0l$, $h = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 22 accurately centered reflections ($9.5^\circ < 2\theta < 18^\circ$). These dimensions and other parameters, including conditions of data collection, are summarized in Table III. Data were collected in the $\theta - 2\theta$ scan mode. Three intense reflections (1,1,3), (3,-1,2) and (3,1,-2) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, $\pm 3\%$, during the course of the experiment. Of the 978 unique reflections measured, 848 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization, but not for absorption effects.¹⁵

Solution and Refinement of the Structure of 2. Atoms were located by use of the heavy-atom method. All calculations were performed on the VAX 11/750

crystallographic computer. All carborane hydrogen atoms were kept in located positions and all xylyl hydrogen atoms were included in calculated positions, C-H = 1.0 Å, with assigned B values of 4.0 and 7.0 Å² for cage and ring and for methyl H, respectively. Anisotropic thermal parameters were refined for Fe and for arene non-hydrogen atoms. Scattering factors for H were obtained from Stewart *et al.*¹⁶ and for other atoms were taken from The International Tables for X-ray Crystallography.¹⁷ Anomalous dispersion terms were applied to the scattering of Fe. A final difference electron density map was essentially featureless, the maximum and minimum peaks being about 0.6 e/Å³. Final positional and thermal parameters for non-hydrogen atoms are given in Table V.

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Supplementary Material Available: Tables of positional and thermal parameters of hydrogen atoms, anisotropic thermal parameters, interatomic distances and angles, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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6. Spectroscopic data : IR spectrum (KBr): 2989(w), 2590(s), 2549(vs), 1458(m), 1397(m), 1183(w), 1164(w), 1091(w), 1025(m), 1011(m), 940(w), 917(m), 822(w), 788(w), 742(w) cm^{-1} . ^1H NMR (ppm, CD_2Cl_2 , 298 K): 3.1 (qtr, 6H, $-\text{CH}_2-$), 2.0 (s, 2H, carborane CH), 1.3 (t, 9H, $-\text{CH}_3$). $^{11}\text{B}\{^1\text{H}\}$ NMR (ppm, THF, 298 K): -12.8, -17.7, -19.8, -22.3, -38.5 (2:3:1:2:1).
7. Spectroscopic data : IR spectrum (KBr): 2984(w), 2544(vs), 1474(m), 1458(m), 1388(s), 1184(w), 1152(m), 1099(w), 1049(w), 1029(w), 1005(s), 975(w), 958(w), 934(w), 835(w), 743(w) cm^{-1} . ^1H NMR (ppm, CD_2Cl_2 , 298 K): 3.2 (qtr, 6H, $-\text{CH}_2-$), 2.3 (s, 1H, carborane CH), 1.9 (s, 1H, carborane CH), 1.3 (t, 9H, $-\text{CH}_3$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (ppm, THF, 298 K): 2.8, -6.0, -17.5, -18.1, -19.4, -26.5, -28.5, -32.6, -38.9 (1:1:1:1:1:1:1:1:1).

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12. C_6 plane- C_2B_3 plane dihedral angles: a) 2.5° in $(\text{CH}_3\text{C}_6\text{H}_5)\text{Fe}[\text{C}_2\text{B}_9\text{H}_9(\text{CH}_3)_2]$. ref 3b. b) 2.9° in $[\text{C}_6(\text{CH}_3)_3\text{H}_3]\text{FeC}_2\text{B}_9\text{H}_{11}$. ref 3a. c) 3.30° in $(\text{C}_5\text{H}_5)\text{FeC}_2\text{B}_9\text{H}_{10}(\text{OCOCF}_3)_8$. Zakharkin, L. I.; Kobak, V. V.; Kovredov, A. I.; Funnanova, N. G.; Struchkov, Y. T. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1979**, 1097 d) 2.08° in $(\text{C}_6\text{H}_6)\text{Fe}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4]$; 2.83° in $[\text{C}_6(\text{CH}_3)_3\text{H}_3]\text{Fe}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4]$. ref 3d. e) 1.2° in $(\text{CH}_3\text{C}_6\text{H}_5)\text{Fe}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4]$. ref 3e.
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Table I. Selected Bond Distances and Angles for 1.

| Bond Distances (Å) | | | | | | | |
|--------------------|-----------|--------------------|-----------|--|--|--|--|
| Fe(03) - C(01) | 2.043(13) | Fe(03) - C(02) | 2.049(13) | | | | |
| Fe(03) - B(04) | 2.082(15) | Fe(03) - B(07) | 2.065(15) | | | | |
| Fe(03) - B(08) | 2.140(14) | Fe(03) - C(31) | 2.09 (2) | | | | |
| Fe(03) - C(32) | 2.082(16) | Fe(03) - C(33) | 2.090(10) | | | | |
| Fe(03) - C(34) | 2.11 (2) | Fe(03) - C(35) | 2.11 (2) | | | | |
| Fe(03) - C(36) | 2.105(11) | C(01) - C(02) | 1.60 (2) | | | | |
| C(01) - B(04) | 1.67 (2) | C(01) - B(05) | 1.70 (2) | | | | |
| C(01) - B(06) | 1.72 (2) | C(02) - B(06) | 1.73 (2) | | | | |
| C(02) - B(07) | 1.69 (2) | C(02) - B(11) | 1.67 (2) | | | | |
| B(04) - B(05) | 1.78 (2) | B(04) - B(08) | 1.76 (2) | | | | |
| B(04) - B(09) | 1.82 (2) | B(07) - B(08) | 1.75 (2) | | | | |
| B(07) - B(11) | 1.80 (2) | B(07) - B(12) | 1.80 (2) | | | | |
| B(08) - B(09) | 1.78 (2) | B(08) - B(12) | 1.81 (2) | | | | |
| Bond Angles (deg) | | | | | | | |
| C(01) Fe(03) C(02) | 46.1(5) | C(01) Fe(03) B(04) | 47.8(6) | | | | |
| C(01) Fe(03) B(07) | 81.9(6) | C(01) Fe(03) B(08) | 82.3(5) | | | | |
| C(01) Fe(03) C(35) | 97.9(6) | C(01) Fe(03) C(36) | 103.6(6) | | | | |
| C(02) Fe(03) B(04) | 82.0(6) | C(02) Fe(03) B(07) | 48.6(5) | | | | |
| C(02) Fe(03) B(08) | 82.9(5) | C(02) Fe(03) C(31) | 100.1(6) | | | | |
| C(02) Fe(03) C(36) | 100.0(6) | B(04) Fe(03) B(08) | 49.3(6) | | | | |
| B(04) Fe(03) C(34) | 92.9(6) | B(04) Fe(03) C(35) | 104.5(6) | | | | |
| B(07) Fe(03) B(08) | 49.3(5) | B(07) Fe(03) C(31) | 100.5(6) | | | | |
| B(07) Fe(03) C(32) | 94.4(6) | B(08) Fe(03) C(32) | 103.5(6) | | | | |
| B(08) Fe(03) C(33) | 92.2(6) | C(31) Fe(03) C(32) | 39.1(6) | | | | |
| C(31) Fe(03) C(36) | 38.9(6) | C(32) Fe(03) C(33) | 39.1(6) | | | | |
| C(33) Fe(03) C(34) | 38.8(6) | C(34) Fe(03) C(35) | 38.6(6) | | | | |
| C(35) Fe(03) C(36) | 38.6(6) | C(02) C(01) B(04) | 111.7(10) | | | | |
| C(01) C(02) B(07) | 109.6(10) | C(01) B(04) B(08) | 106.4(10) | | | | |
| C(02) B(07) B(08) | 107.1(10) | B(04) B(08) B(07) | 105.0(10) | | | | |

Table II. Selected Bond Distances and Angles for 2.

| Bond Distances (Å) | | | | | | | |
|--------------------|------------|--------------------|-----------|--|--|--|--|
| Fe(03) - C(01) | 2.040(10) | Fe(03) - C(02) | 2.044(11) | | | | |
| Fe(03) - B(04) | 2.116(11) | Fe(03) - B(07) | 2.104(13) | | | | |
| Fe(03) - B(08) | 2.110(11) | Fe(03) - C(31) | 2.130(9) | | | | |
| Fe(03) - C(32) | 2.095(9) | Fe(03) - C(33) | 2.094(9) | | | | |
| Fe(03) - C(34) | 2.132(9) | Fe(03) - C(35) | 2.113(9) | | | | |
| Fe(03) - C(36) | 2.127(9) | C(01) - C(02) | 1.633(13) | | | | |
| C(01) - B(04) | 1.706(14) | C(01) - B(05) | 1.721(16) | | | | |
| C(01) - B(06) | 1.742(16) | C(02) - B(06) | 1.719(15) | | | | |
| C(02) - B(07) | 1.706(15) | C(02) - B(11) | 1.700(15) | | | | |
| B(04) - B(05) | 1.797(15) | B(04) - B(08) | 1.772(15) | | | | |
| B(04) - B(09) | 1.752(15) | B(05) - B(06) | 1.745(17) | | | | |
| B(05) - B(09) | 1.736(15) | B(05) - B(10) | 1.736(16) | | | | |
| B(06) - B(10) | 1.764(15) | B(06) - B(11) | 1.783(16) | | | | |
| B(07) - B(08) | 1.797(17) | B(07) - B(11) | 1.788(17) | | | | |
| B(07) - B(12) | 1.760(17) | B(08) - B(09) | 1.806(15) | | | | |
| B(08) - B(12) | 1.808(15) | B(09) - B(10) | 1.746(15) | | | | |
| B(09) - B(12) | 1.777(15) | B(10) - B(11) | 1.791(16) | | | | |
| B(10) - B(12) | 1.811(15) | B(11) - B(12) | 1.757(15) | | | | |
| C(31) - C(32) | 1.404(13) | C(31) - C(36) | 1.416(14) | | | | |
| C(31) - C(37) | 1.523(17) | C(32) - C(33) | 1.417(14) | | | | |
| C(33) - C(34) | 1.430(16) | C(34) - C(35) | 1.379(13) | | | | |
| C(34) - C(38) | 1.515(15) | C(35) - C(36) | 1.427(14) | | | | |
| Bond Angles (deg) | | | | | | | |
| C(01) Fe(03) C(02) | 47.14(38) | C(01) Fe(03) B(04) | 48.40(41) | | | | |
| C(01) Fe(03) B(07) | 83.90(46) | C(01) Fe(03) B(08) | 83.76(40) | | | | |
| C(01) Fe(03) C(35) | 100.39(36) | C(01) Fe(03) C(36) | 98.31(38) | | | | |
| C(02) Fe(03) B(04) | 82.56(44) | C(02) Fe(03) B(07) | 48.53(41) | | | | |
| C(02) Fe(03) B(08) | 83.39(42) | C(02) Fe(03) C(31) | 96.80(41) | | | | |
| C(02) Fe(03) C(36) | 103.99(40) | B(04) Fe(03) B(08) | 49.59(40) | | | | |
| B(04) Fe(03) C(34) | 94.76(43) | B(04) Fe(03) C(35) | 98.95(43) | | | | |

Table II. continued

| | | | | | | | |
|--------|--------|-------|------------|-------|--------|-------|-------------|
| B(07) | Fe(03) | B(08) | 50.48(46) | B(07) | Fe(03) | C(31) | 104.93(45) |
| B(07) | Fe(03) | C(32) | 91.19(45) | B(08) | Fe(03) | C(33) | 91.53(42) |
| B(08) | Fe(03) | C(34) | 101.95(41) | C(31) | Fe(03) | C(32) | 38.80(35) |
| C(31) | Fe(03) | C(36) | 38.85(37) | C(32) | Fe(03) | C(33) | 39.54(39) |
| C(33) | Fe(03) | C(34) | 39.53(42) | C(34) | Fe(03) | C(35) | 37.91(35) |
| C(35) | Fe(03) | C(36) | 39.34(40) | C(02) | C(01) | B(04) | 110.60(82) |
| C(01) | C(02) | B(07) | 112.13(87) | C(01) | B(04) | B(08) | 105.63(77) |
| C(02) | B(07) | B(08) | 104.18(86) | B(04) | B(08) | B(07) | 107.42(77) |
| Fe(03) | C(31) | C(37) | 130.55(87) | C(32) | C(31) | C(36) | 120.00(88) |
| C(32) | C(31) | C(37) | 120.16(89) | C(36) | C(31) | C(37) | 119.74(84) |
| C(31) | C(32) | C(33) | 120.25(92) | C(32) | C(33) | C(34) | 119.79(88) |
| Fe(03) | C(34) | C(38) | 131.29(72) | C(33) | C(34) | C(35) | 119.37(96) |
| C(33) | C(34) | C(38) | 119.02(94) | C(35) | C(34) | C(38) | 121.55(108) |
| C(34) | C(35) | C(36) | 121.49(92) | C(31) | C(36) | C(35) | 119.02(83) |

Table III. Details of Crystallographic Data collection.

| compound | 1 | 2 |
|---|--|--------------------------------------|
| temp/K | 298 | 298 |
| crystal size/mm | 0.13 x 0.26 x 0.45 | 0.2 x 0.3 x 0.4 |
| normal to faces | 10 $\bar{1}$, 103, 010 | 100, 010, 001 |
| appearance | parallelepiped | parallelepiped |
| radiation (graphite monochromator) | Mo K α | Mo K α |
| wavelength/Å | 0.7107 | 0.7107 |
| space group | <i>P2₁/c</i> | <i>Pna2₁</i> |
| <i>a</i> /Å | 7.7452(7) | 12.862(3) |
| <i>b</i> /Å | 8.8974(9) | 7.491(2) |
| <i>c</i> /Å | 19.6596(20) | 15.002(3) |
| β /deg | 90.195(3) | |
| <i>V</i> /Å ³ | 1355 | 1445 |
| <i>Z</i> | 4 | 4 |
| ρ (calcd)/g cm ⁻³ | 1.37 | 1.35 |
| μ /cm ⁻¹ | 10.8 | 10.2 |
| scan width, below <i>K</i> α ₁ | 1.3 | 1.3 |
| above <i>K</i> α ₂ | 1.6 | 1.6 |
| scan rate/deg min ⁻¹ | 3.0 | 3.0 |
| number of unique reflections | 2386 | 978 |
| number of observed (<i>I</i> > 3 σ (<i>I</i>)) reflections | 1588 | 848 |
| 2 θ max/deg | 50 | 45 |
| data collected | + <i>h</i> , + <i>k</i> , \pm <i>l</i> | + <i>h</i> , + <i>k</i> , + <i>l</i> |
| number of parameters refined | 148 | 125 |
| <i>R</i> | 0.08 | 0.045 |
| <i>R_w</i> | 0.11 | 0.056 |
| <i>GOF</i> | 3.49 | 1.81 |

Table IV. Positional and Equivalent Isotropic Thermal Parameters for 1.

| Atom | x | y | z | <u Squared> |
|-------|------------|-------------|------------|-------------|
| Fe(1) | 0.2495(3) | 0.1931(1) | 0.9035(1) | 0.065 |
| B(08) | 0.2490(17) | -0.0465(16) | 0.9127(7) | 0.066 |
| C(02) | 0.3523(16) | 0.1465(15) | 0.8099(6) | 0.073 |
| B(04) | 0.0682(19) | 0.0345(18) | 0.8722(7) | 0.074 |
| B(07) | 0.4284(18) | 0.0350(17) | 0.8729(7) | 0.070 |
| C(01) | 0.1453(17) | 0.1447(16) | 0.8104(7) | 0.074 |
| B(10) | 0.2486(23) | -0.1374(22) | 0.7711(9) | 0.084 |
| B(12) | 0.3657(22) | -0.1535(20) | 0.8497(9) | 0.081 |
| B(09) | 0.1399(21) | -0.1533(19) | 0.8490(8) | 0.078 |
| B(11) | 0.4257(21) | -0.0213(20) | 0.7847(8) | 0.081 |
| B(05) | 0.0639(21) | -0.0240(20) | 0.7855(8) | 0.085 |
| B(06) | 0.2462(23) | 0.0511(21) | 0.7455(9) | 0.088 |
| C(36) | 0.268(3) | 0.429(1) | 0.9033(5) | 0.035(4) * |
| C(35) | 0.103(3) | 0.388(1) | 0.9247(5) | 0.063(6) * |
| C(34) | 0.083(3) | 0.284(1) | 0.9773(5) | 0.069(6) * |
| C(33) | 0.229(3) | 0.222(1) | 1.0086(5) | 0.050(5) * |
| C(32) | 0.393(3) | 0.263(1) | 0.9872(5) | 0.053(5) * |
| C(31) | 0.413(3) | 0.367(1) | 0.9346(5) | 0.055(5) * |
| C(21) | 0.182(5) | 0.424(2) | 0.904(1) | 0.03(1) * |
| C(22) | 0.360(5) | 0.406(2) | 0.911(1) | 0.06(1) * |
| C(23) | 0.427(5) | 0.309(2) | 0.961(1) | 0.14(2) * |

Table IV. (continued)

| Atom | x | y | z | <u Squared> |
|--------|------------|-----------|-----------|-------------|
| C(24) | 0.315(5) | 0.229(2) | 1.003(1) | 0.03(1) * |
| C(25) | 0.137(5) | 0.246(2) | 0.996(1) | 0.05(1) * |
| C(26) | 0.070(5) | 0.344(2) | 0.946(1) | 0.07(1) * |
| C(37) | 0.604(3) | 0.390(3) | 0.916(1) | 0.10(1) * |
| C(37') | -0.107(4) | 0.386(4) | 0.918(2) | 0.07(1) * |

Carbons from C(31) to C(37) are of the arene in the position of major occupancy.

Carbons from C(21) to C(26) and C(37') belong to the disordered arene in the position of lower occupancy. Units of <u Squared> are Å². Units of each E.S.D., in parentheses, are those of the least significant digit of the corresponding parameters. * Denotes an atom refined with an isotropic thermal parameter. Other isotropic values are $[1 / 8 \pi^2]$ times the "equivalent B value" for an anisotropic atom, as defined by W. C. Hamilton (1959) Acta Cryst. 12, 609-610.

Table V. Positional and Equivalent Isotropic Thermal Parameters for 2.

| Atom | x | y | z | Ux10E4 |
|--------|-------------|--------------|-------------|----------|
| Fe(03) | 0.1710(1) | 0.0889(1) | 0.0000 | 320(6) |
| C(01) | 0.2203(8) | 0.2532(14) | -0.0999(6) | 437(25)* |
| C(02) | 0.2011(8) | 0.0476(14) | -0.1322(7) | 433(25)* |
| B(04) | 0.1125(8) | 0.3350(14) | -0.0478(8) | 389(25)* |
| B(05) | 0.1416(9) | 0.3923(15) | -0.1614(8) | 448(29)* |
| B(06) | 0.2014(9) | 0.2105(16) | -0.2129(9) | 477(29)* |
| B(07) | 0.0817(10) | -0.0299(18) | -0.1014(8) | 454(34)* |
| B(08) | 0.0216(8) | 0.1572(13) | -0.0470(8) | 387(24)* |
| B(09) | 0.0166(8) | 0.3303(15) | -0.1307(7) | 424(26)* |
| B(10) | 0.0688(8) | 0.2571(16) | -0.2317(8) | 454(28)* |
| B(11) | 0.1101(8) | 0.0315(15) | -0.2140(8) | 431(28)* |
| B(12) | -0.0049(8) | 0.1048(14) | -0.1624(7) | 403(25)* |
| C(31) | 0.2669(7) | -0.1205(13) | 0.0497(6) | 430(57) |
| C(32) | 0.1634(7) | -0.1441(13) | 0.0770(6) | 431(55) |
| C(33) | 0.1097(8) | -0.0040(15) | 0.1207(6) | 445(63) |
| C(34) | 0.1613(8) | 0.1618(15) | 0.1371(6) | 457(59) |
| C(35) | 0.2617(8) | 0.1855(14) | 0.1071(7) | 491(64) |
| C(36) | 0.3169(7) | 0.0457(14) | 0.0631(6) | 451(60) |
| C(37) | 0.3237(7) | -0.2698(14) | 0.0009(13) | 671(59) |
| C(38) | 0.1024(10) | 0.3104(16) | 0.1834(8) | 741(86) |

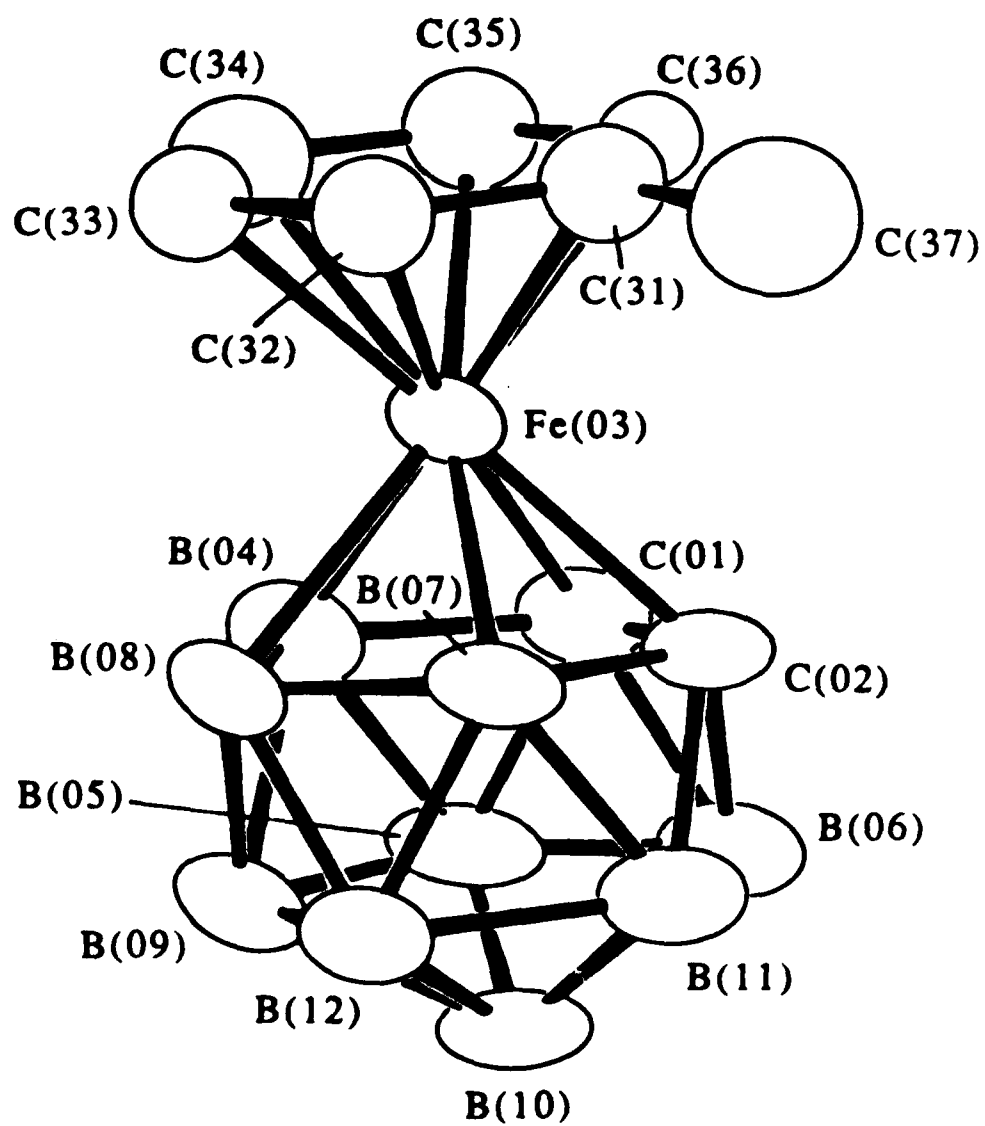
$U_{eq} = [1/6 \pi^2] \times \sum \sum \beta_{ij} a_i a_j$. * Denotes an atom refined with an isotropic thermal parameter.

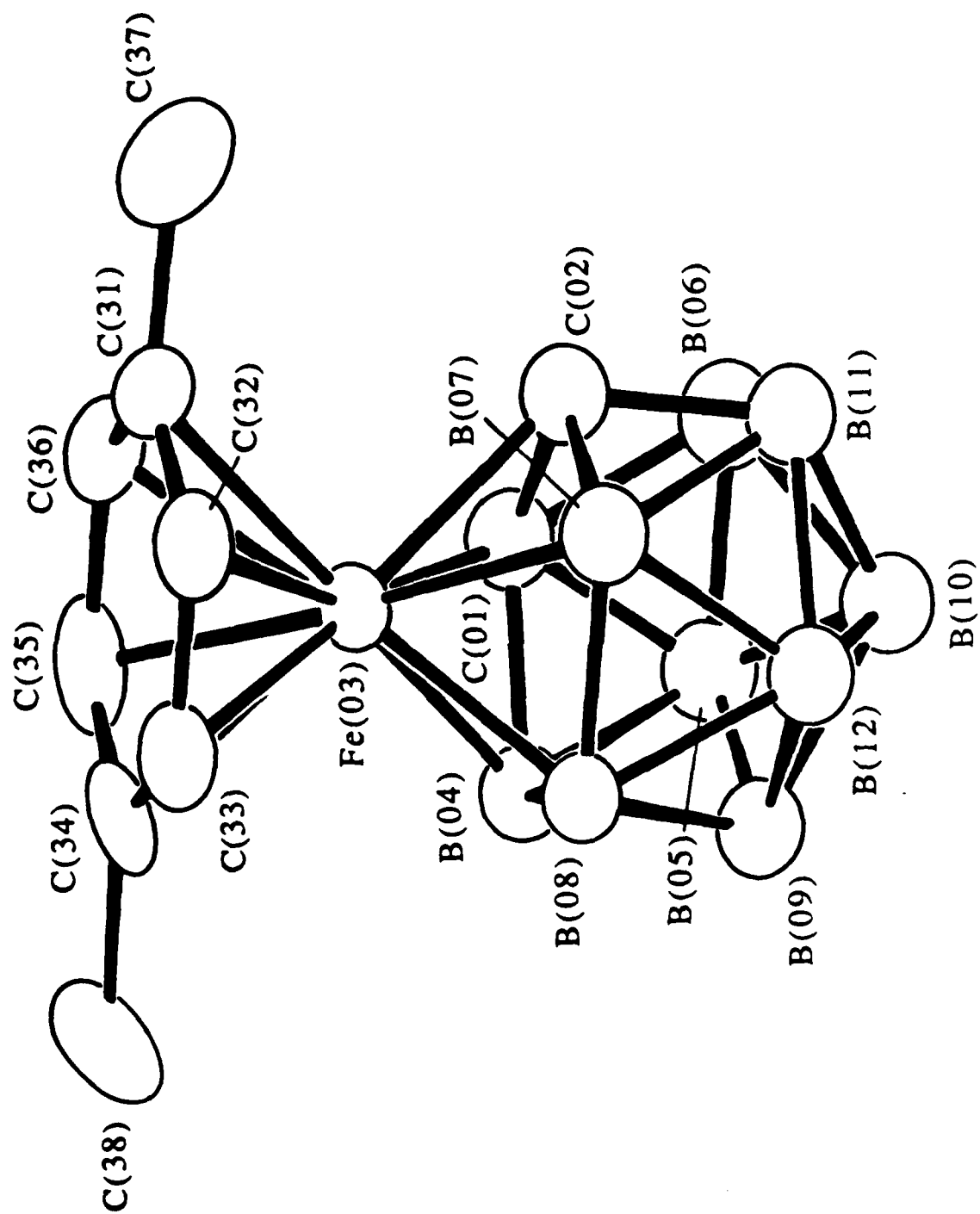
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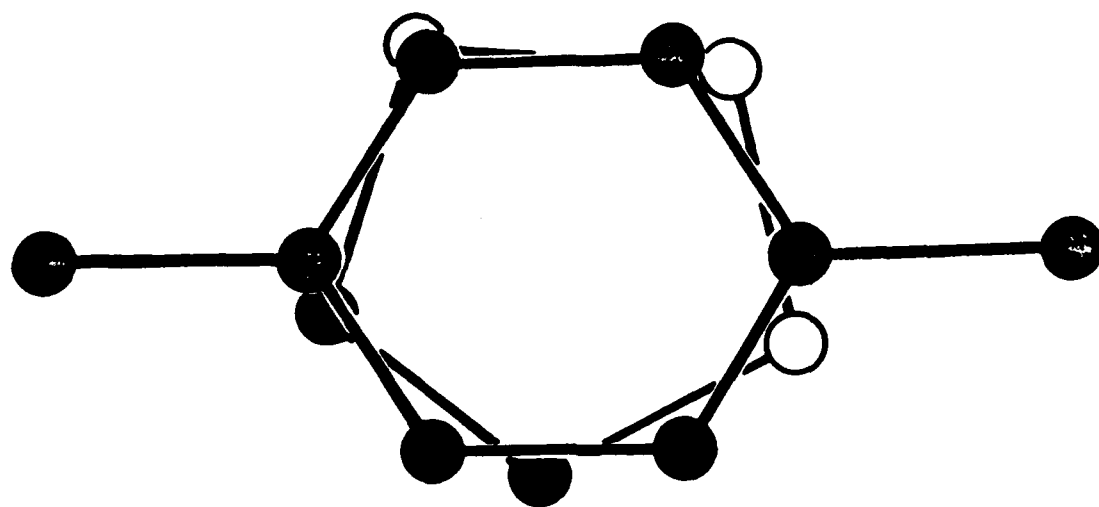
Figure 1. Molecular structure of *closo*-3-(η^6 -CH₃C₆H₅)-3,1,2-FeC₂B₉H₁₁(1) showing atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

Figure 2. Molecular structure of *closo*-3-(η^6 -1,4-(CH₃)₂C₆H₄)-3,1,2-FeC₂B₉H₁₁(2) showing atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

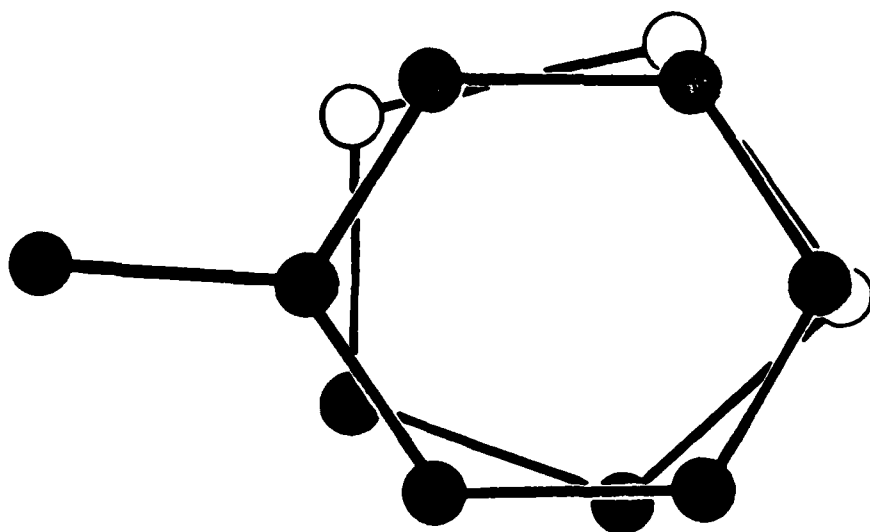
Figure 3. Projections of arene rings onto carborane C₂B₃ planes.







● C ○ B



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